Fuel Soot Monitoring by Light Extinction Measurement (LEM®)

David N. Yunkers
Analysts, Inc.
12715 Royal Drive
Stafford, Texas 77477
(800) 248-7778

1998

Abstract: Fuel soot is the primary contaminant in diesel engine lubricants. Evolving emission regulations, engine designs and oil formulations are all centered around the control and retention of soot particles and advanced gel formations. Accurate, reliable and cost effective measurement of soot is now an essential requirement for an effective oil analysis program.

Key Words: Agglomerations; Dispersant additives; Fuel soot; Interferences; Light Extinction Measurement (LEM); Thermogravimetric Analysis (TGA).

Introduction: Fuel soot is formed during the normal combustion processes in diesel engines. These soot particles will vary in size and shape. The rate at which soot is generated is also variable and dependant upon many factors. The factors that affect the creation of soot can include:

- Engine type, size and configurations.
- Equipment applications, operating modes and frequencies.
- Fuel delivery and control settings.
- Intake, exhaust and EGR conditions.
- Wear modes of the engine and fuel delivery components.
- Equipment age.

During engine operations, soot particles are either emitted within the exhaust, retained in the combustion chamber, or transferred into the engine's lube oil via blow-by and wash-down within the oil film on the cylinder/liner surfaces (thermophoresis). Soot particles and formations comprise the largest volume of contamination present in used diesel engine oils.

Regardless of disposition, soot is an undesirable element that creates problems for equipment owners, operators and maintenance personnel:

1. Exhausted soot is an environmental pollutant.
2. Soot retained in combustion areas contributes to deposit formations.
3. Soot that enters the crankcase depletes oil additives, forms gels that thicken the oil and evolves into hard deposits that promote wear!

Internal control of these soot formations is accomplished by dispersant lube oil additives. These dispersants are charged with preventing gel formation, conveying larger formations to the filter for removal, and retaining the smaller unfiltered particles in suspension.

Discussion: In addition to problems and influences fuel soot has presented in the past, we are now contending with even greater soot levels. The U.S. Federal Heavy-Duty Diesel Emission Standards, as well as state and local regulations, have included stronger controls of engine exhaust emissions.

To meet these new standards, one area of major change in equipment designs have been through increased usage of exhaust gas recirculation (EGR) systems. Recirculating systems will decrease emissions. However, they also increase the soot levels deposited into the lube oils (estimated at typically +15%) increasing the demand upon dispersant additives and diminishing the performance and safe life of lube oils.

These changes have also placed greater demand upon oil testing programs to provide accurate and reliable information for safely controlling oil and filter service intervals. Lube oil testing programs include many different tests in attempts to segregate and measure representations of soot in the lube oil. However, soot is an evolving compound of carbon and hydrogen that has varying structures which are present in more than one form or "stage". Coupling this with the reactions and combined effects of other oil properties and conditions creates major limitations in accurately measuring soot levels.

Standard tests available for measuring soot levels have not been capable of segregating and accurately detecting the actual minute soot particles. Most methods rely on the use of a dilution agent (solvent) to "release" suspended soot from within an oil and then centrifuging the sample to determine the level of soot present (represented mass).

Based on the assumption that the majority of particulate being removed is soot, these methods were effective for the given times, products and purposes. However, due to greatly improved dispersant used in today's engine lube oils, the agents used in these testing procedures can no longer remove all of the particulate for accurate and reliable measurements!

Test Methods: A summary of the test methods most commonly used in oil analysis programs is as follows:

• **Total Solids:** There are many variations of this test used to obtain a representation of the "total solids" present in lube oil. Typically, a sample is diluted with a solvent, centrifuged to remove any particulate, and the result is applied as a representation of soot levels. These tests cannot segregate and measure soot alone. They can only express a representation of the *total contaminants* that are: (1) Not suspended within the oil and (2) That can be released or "stripped" from the dispersant additives.

The obvious limitation is that the extracted "solids" can also include: Oxidized oil products, sand or dirt, wear metals, gasket, seal or hose materials, filter media or fibers, paint chips, water and any other solid foreign materials that may enter the engine.

However, the major limitation of these tests lies within the current generation of engine oils; Many dispersant additives are so effective, the soot particles and formations cannot be adequately released, extracted and measured.

• **Soot (Abs) by Infrared:** Infrared (FT-IR) analysis [1] is the most common test performed for expressing a specific "Fuel Soot" level and has been used within the lube testing industry for many years. The main criterion for using infrared is the low cost of performing the analysis and several other properties and contaminants can be measured within the same procedure.

Infrared does not measure any organic presence relative to soot. Infrared operates through the function of light transmission through a fluid sample and the assumption is that only soot particles will absorb or block out the infrared light [1,2].

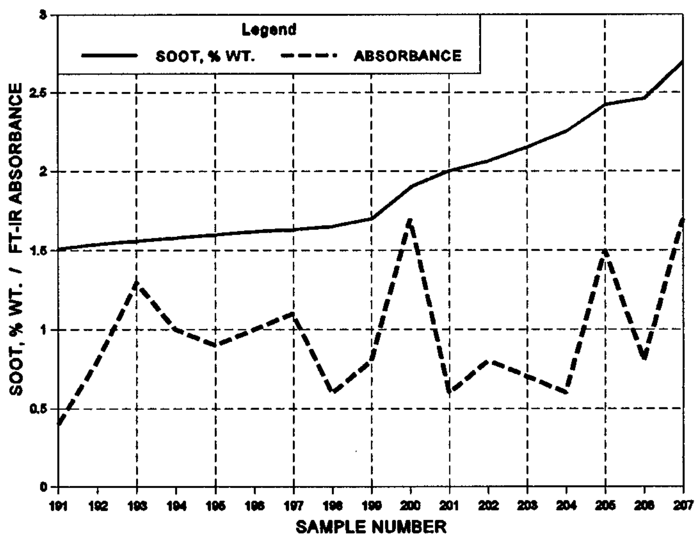

Figure I. Examples of light scattering affects upon samples with soot greater than 1.5% wt.

Soot particles are actually "black carbon" and high concentrations can totally "block out" the infrared light transmission, limiting the detection range. Since soot is basically carbon, wear metals and oxidation products in the oil can become adsorbed onto soot particles. Also, the presence of gels within soot formations can distort the light transmission, resulting in "light scattering" [3]. These interferences greatly affect both accuracy and repeatability.

There are many types of IR instruments that operate on similar principles. However, these instruments do not always produce equal or comparable results. Nor are there any common "soot standards" available for calibration and/or standardization. Results are typically reported in units of absorbance (ABS) which are not converted or related to an actual percent of mass or volume [1,2,3].

Our research has shown that IR can be a relatively acceptable indicator, providing the soot is present in "normal to moderate" (<1.5%) levels. When higher levels of soot that are important to the evaluation of the engine and lube oil are present, the implied soot levels by infrared detection (ABS) *can actually decrease* due to the presence of gels and agglomerated soot masses.

• **Pentane Insolubles:** When properly performed by ASTM D893 [4], pentane insolubles (PI) are applied as a representation of agglomerated soot (masses) for an indicator of the oil's dispersant (additive) efficiency. The complexity of this procedure prohibits it's use and application in a production laboratory environment.

This test is more accurate and reliable than a "total solids" test but does not measure, nor account for, the total (dispersed) soot particles present. This method actually measures the affects of already failed or "tied up" dispersant. At this point gels, sludge and deposits may have already formed within the engine.

• **Thermogravimetric Analysis (TGA):** TGA represents the weight change of a material as a function of temperature during thermal processing. As performed on used diesel engine oil, TGA measures the carbon present within the sample. Since soot is basically carbon (though not completely), TGA has been the most accurate representation of soot available for many years. Both the complexity and costs of this procedure prohibits it's use and application in a production laboratory environment.

Even TGA has limitations; TGA results can be affected by the presence of hydrocarbons. Carbon is a major ingredient in both diesel fuels and crankcase oils. Most diesel engine oils also contain calcium carbonate (additives) which can affect the test results [3]. Good reference oil's are required for TGA analyses.

Analysts' Commitment: Analysts, Inc. has been an innovating leader in lube oil analysis for over 37 years. We have always been aware of the value and importance of accurate soot detection and monitoring for diesel engines. We have utilized all of the fore-mentioned testing procedures in our efforts to provide the best services possible. Time has reflected many changes:

1. Lube oil additives have surpassed the ability of simple extraction tests being able to remove the soot for measurement. The levels of soot being inducted and retained within the oils have surpassed the abilities of IR to be an applicable indicator.

2. The cost of lube oils, as well as storage, handling and disposal has increased considerably.

Maximum safe utilization of our oil is "a must" for profitable equipment operation.

3. Engine manufacturers are being required to modify equipment and develop new designs that reduce emissions. These changes are not just reflected in increased costs for new equipment, but the costs of routine operations, maintenance, repair and replacements have also escalated.

Just as insufficient services can be costly in engine wear and component repair or replacements, premature services can also be very costly. A major contributor toward control of these costs is an accurate and affordable means of monitoring soot levels to determine whether the oil is adequately dispersing the soot particles and at what point are the oil's additives being "loaded" and require replacement.

Important as this information has always been, it is even more crucial for the engines of today and tomorrow. With this in mind, Analysts, Inc. charged it's Research and Development Group with the challenge of developing a means of *specifically measuring dispersed soot* in diesel engine oils. The requirements included:

1. Accuracy that was free of the interferences of present methods.
2. Measurement without the need of specific reference oils.
3. Dynamic range of detection.
4. Repeatability.
5. Cost effective production for routine oil analysis programs.

Light Extinction Measurement (LEM): In 1993 Analysts' Research and Development Group, under the direction of Dr. William Seifert and Vernon Westcott (founding developers of Ferrographic Analysis), succeeded in our quest to provide a reliable and affordable means of detection and measurement of dispersed soot within used diesel engine oils.

The instrument developed utilizes the methodology of Light Extinction Measurement [3], hence the name LEM®. The method qualifies in all the fore mentioned requirements and has proven to be so revolutionary, it provides data that has never before been so readily available!

LEM detection [3] is the extension coefficient of the fluid to the passage of broad band light. White light is used to avoid molecular resonances of compounds. Dispersed soot particles are measured in ranges from a few nanometers in diameter to typically 200 nanometers. Should a degree of resonances appear, the broad band (white light) eliminates any significant error.

The detection and measurement of the actual soot particles (spheres) is accomplished "directly within the sample"[3]. LEM does not rely upon solvent dilutions to release the particulate, separation of "solids" by a centrifuge, flame or heat to consume the sample, nor transmission of an infrared light through the sample.

The later point is extremely important. The "soot load" of many oils is too high to allow passage of an infrared light transmission. As soot gels and forms agglomerations, infrared transmission is further "blocked" by the total of the formed masses. LEM detects the actual dispersed soot particles and the broad band white light is not deterred by the presence of gel within the formations. Where extreme levels of soot are present and/or the soot has been allowed to agglomerate due to depleted dispersant, the introduction of fresh dispersant additives provides the means for unlimited measurement capabilities (Based on the principle of Lambert-Beers Law [5]).

The measurements are relative to the mass and reported in percentages (% mass) that can be reliably applied to OEM recommended guidelines for maximum allowable soot as determined by TGA.

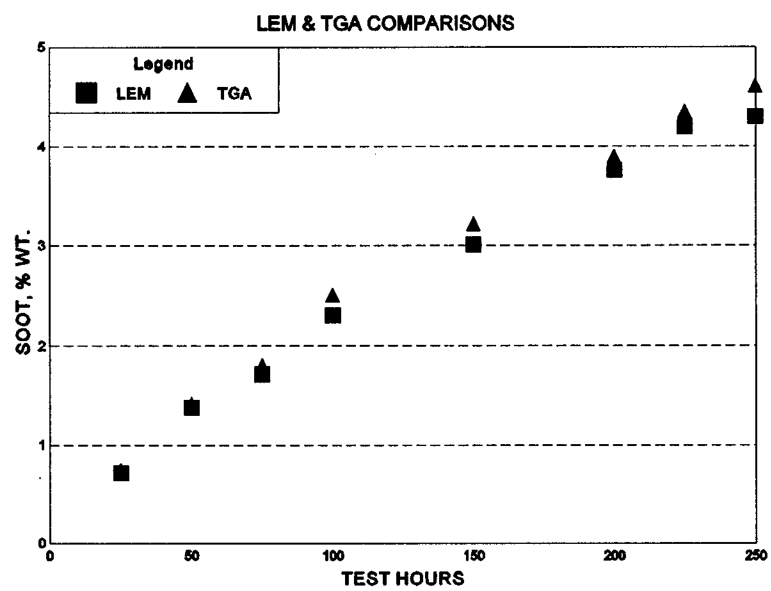

Figure II. Comparison of LEM and TGA data through a MACK T-8 engine soot test.

Confirmations: The development of LEM was accomplished with the cooperation and assistance of several lubricant, additive and engine manufacturers. LEM instrumentation was installed on-site within Chevron Research (CRTC) and Detroit Diesel's Central Chemical Laboratory. Other participants included Pennzoil Research, Lubrizol Corporation and Mack Engineering.

During the initial installation at DDC, the LEM was stringently compared to results obtained from their own TGA lab[6]. The regression output of LEM to TGA was $R^2 = 0.998$! This is quite remarkable, especially where two different methodologies are employed. In such studies, a factor of $R^2 = 0.80$ can be considered sound and acceptable.

Additional accuracy and repeatability studies were performed within the DDC Central Laboratory and in 1994 the report at the conclusion of their research stated "The data generated qualifies LEM (Light Extinction Measurement) to be used as an alternative to TGA [6] for measurement of soot in used engine oils....". Their report further stated "The other key factor" related to the productivity of LEM which within their own lab was "evaluated as LEM:TGA::8:1."

Pennzoil's Research Laboratory compared Analysts' application of LEM results toward dispersant additive effectiveness and depletion. The results obtained within their lab confirmed the accuracy and dependability of our interpretations.

In 1995 Mack Engineering Group [7] re-established their soot limitations within Mack engines. The new guideline of acceptability to 4.0% specifies "determination by LEM."

Conclusion:

Analysts' Light Extinction Measurement (LEM) for diesel fuel soot analysis is at minimum, equal to the most accurate means available (TGA) to date. LEM requires no special reference oils or standards to perform the analyses. The production capabilities of LEM allows Analysts, Inc. to provide precise data and interpretations to clients without timely delays or exorbitant cost.

References:

1. **Powell, J.R. and Compton, D.A.C.** - Automated FTIR Spectrometry for Monitoring Hydrocarbon Based Engine Oils, Lubrication Engineering, STLE, March 1993, pp233-239.

2. **Seifert, W. W. and Dejardins, J. B.** - An Improved Method for measuring the Amount of Soot in Diesel Lubricating Oil, Condition Monitoring 94 Conference, Ed. Jones, M. H., Pineridge Press, 1994.

3. **Seifert, W. W. and Dejardins, J. B.** - Test Results Obtained by LEM, TGA and IR for Measuring Soot in Diesel Oil, Condition Monitoring 94 Conference, Ed. Jones, M. H., Pineridge Press, 1994.

4. Standard Test Method for Insolubles in Used Lubricating Oils, Annual Book of ASTM Standards, Vol. 05.01, 1995, pp 272-276.

5. Van Norstrand's Scientific Encyclopedia, Sixth Edition, Van Norstrand Reinhold Co., New York 1983, pp. 327.

6. **Peiris, Suran** - Comparison of LEM and TGA Techniques for the Measurement of Soot in Used Engine Oils, DDC Central Laboratory Project, 1994.

7. **Mack Trucks, Inc** - Engine Oil Analysis Soot Specification, Service Bulletin 91D022, Ed. Service Publications, 1996.